Finally, the catalyst becomes covered almost completely with ethylene, to the exclusion of hydrogen.

Hydrogenation thus takes place comparatively slowly by collision between adsorbed ethylene and hydrogen or by diffusion of hydrogen to the catalyst surface through a thin layer of ethylene.

It will be noticed that the " induction " period is reduced in a very marked way either by increase of ethylene-content in the gas mixture or by increase in temperature, while the rate of reaction after the maximum has been reached is only very slightly affected by temperature. These observations are in accordance with the above theory. The final rate of reaction falls off gradually, owing to the accumulation in the reaction tube of inert ethane which acts as a diluent to the gas mixture.

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## The Catalytic Activity of Copper.—Part II.

By William George Palmer, St. John's College, Cambridge.

In Part I of this series of papers,[*] the writer described the construction of an apparatus for determining directly the relation between reaction-velocity and temperature in the catalytic dehydrogenation of ethyl alcohol by the action of copper produced from cupric oxide by reduction. Some preliminary results were also given. This work has now been extended both by using reducing agents other than hydrogen (namely, carbon monoxide and methyl alcohol vapour) in the preparation of the catalyst and by the use of other alcohols as reacting substances.

In the earlier work, the method consisted in obtaining an automatic record of the rate of escape of hydrogen liberated in the reaction, at several different temperatures, the temperature being kept constant during each experiment. This method proved very laborious, since only by making experiments at a great number of different temperatures could a sufficiently intimate knowledge of the influence of temperature be obtained. Also, the catalyst had always to be reprepared by oxidation and reduction between experiments.

It has now been found possible to obtain a continuous record of the change of activity, while the temperature of the reaction is gradually increasing through the range to be studied.

[*] ' Roy. Soc. Proc.,' A, vol. 98, p. 13.

The gas-meter described in the former paper was not found suitable for the record of changing rates in the escape of hydrogen. After some tentative experiments, the following simple arrangements of recording apparatus were adopted. The hydrogen liberated in the reaction tube passed first into a flask of 1 litre capacity, kept surrounded with cold water, to secure temperature control of the gas, and thence to the gas-meter, which was very simply constructed of a glass tube, with a wide, salver-shaped end dipping into a wider vessel nearly filled with water.

With a head of water of 2 cm., the relation summarised below was found between the capacity of the meter and the rate of flow of gas.

| Time in seconds for escape of 10 bubbles. | Size of bubbles in c.c. | Time in seconds for escape of 10 bubbles. | Size of bubbles in c.c. |
|---|---|---|---|
| 12 ·8 | 2 ·18 | 70 ·0 | 1 ·86 |
| 17 ·2 | 2 ·05 | 93 ·0 | 1 ·84 |
| 56 ·8 | 1 ·87 | | |

Thus the capacity of the meter is practically constant if a rate of flow of ten bubbles in one minute is not exceeded : the maximum rate of flow of hydrogen in any experiment was never greater than nine bubbles per minute.

The electrolytic manometer before described (*loc. cit.*) was again used, but not, in the present experiments, to actuate the chronograph directly. The electrodes were arranged as part of a telephone circuit in such a way that contact was made just before a bubble was released, and sharply broken at the release by the descent of the sulphuric acid. Immediately the " break " was heard in the telephone, a key was depressed by hand to actuate the chronograph, and, as nearly as possible at the same instant, the temperature was read on the millivoltmeter. Owing to the use of this telephone device, visual attention could be wholly concentrated on the accurate reading of the temperature. As the temperature reached its upper limit, it became necessary to record several bubbles as one on the chronograph to avoid having readings too close together, so that it was not possible to form a completely automatic record as formerly.

From the chronograph record two curves were constructed, one showing the relation between temperature and time, and the other that between reaction-velocity and time. It was then easy to make a simple reaction-velocity temperature curve from these two auxiliary curves. The exactness in coincidence on the two auxiliary curves of a temporary fall in temperature, with a corresponding fall in reaction-velocity, demonstrated the nicety with which the two curves were " in register."

The catalyst used in all the experiments was the same as that used in the work described before. At the close of the experiments, the copper was removed by solution in nitric acid, and estimated electrolytically as 0·022 grm.

A. *Reduction of the Oxide with Carbon Monoxide : Anhydrous Ethyl Alcohol as Reacting Substance.*

The carbon monoxide was prepared by passing carbon dioxide over strongly heated wood-charcoal. The resulting gas was passed through a long tube containing reduced copper at 300° C., to remove any possible contamination. The purified gas was stored in aspirators containing water, from which dissolved air had been removed by a current of carbon dioxide.
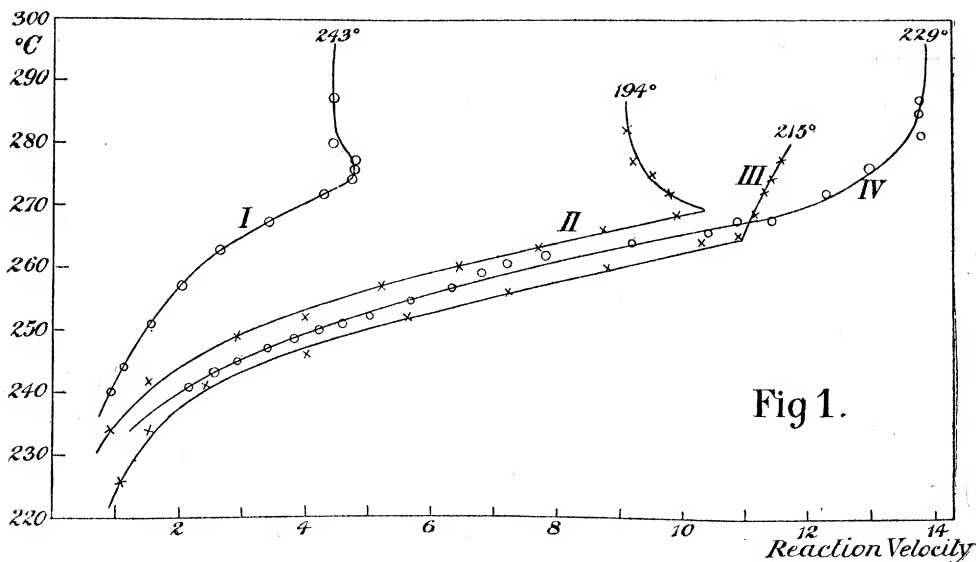
Experiments were conducted in a way almost exactly similar to those in which hydrogen was used as reducing agent. The apparatus was filled with pure dry nitrogen instead of with carbon dioxide as formerly.

The necessary increase of sensitiveness in the millivoltmeter was obtained by using a bath of boiling ethyl benzoate (boiling point 213° C.) for the constant temperature junction, and an external resistance was dispensed with. An auxiliary couple in a boiling water bath was used to determine reduction temperatures below 213° C. The period of heating from about 230° C. to 300° C. was usually about one and a quarter hour. The reduction of the copper oxide was always signalised by a " kick " on the millivoltmeter needle over about 4° C. The mean between the highest temperature reached and the initial temperature was taken as the temperature of reduction.

Table I.—Catalyst prepared by reduction with Carbon Monoxide : Anhydrous Ethyl Alcohol as Reacting Substance.

(1) Temperature of Reduction 215° C. (Curve III, fig. 1.)

| Temperature. | Volume of hydrogen in 30 seconds. | Gramme-molecules of alcohol decomposed per second per gramme-atom of copper $\times 10^3$. | |
| --- | --- | --- | --- |
| ° abs. | c.c. | Observed. | Calculated. |
| 499 | 1 ·1 | 4 ·77 | 3 ·32 |
| 507 | 1 ·5 | 6 ·50 | 6 ·30 |
| 514 | 2 ·4 | 10 ·4 | 10 ·8 |
| 519 | 4 ·0 | 17 ·3 | 15 ·9 |
| 525 | 5 ·6 | 24 ·3 | 24 ·1 |
| 529 | 7 ·2 | 31 ·2 | 31 ·2 |
| 533 | 8 ·8 | 38 ·2 | 42 ·0 |
| 537 | 10 ·3 | 44 ·6 | 44 ·6 |
| 538 | 10 ·9 | 47 ·3 | |
| 539 | 11 ·0 | 47 ·7 | |
| 541 | 11 ·1 | | |
| 545 | 11 ·3 | | |
| 550 | 11 ·6 | | |
| 559 | 12 ·5 | | |

(2)  Temperature of Reduction 243° C.   (Curve I, fig. 1.)

| Temperature. | Volume of hydrogen in 30 seconds. | Gramme-molecules of alcohol decomposed per second per gramme-atom of copper × $10^3$. | |
|---|---|---|---|
| ° abs. | c.c. | Observed. | Calculated. |
| 513 | 0·9 | 4·32 | 3·7 |
| 517 | 1·1 | 4·77 | 4·3 |
| 524 | 1·5 | 6·50 | 6·5 |
| 530 | 2·0 | 8·66 | 8·7 |
| 536 | 2·6 | 11·20 | 12·0 |
| 540 | 3·4 | 14·70 | 14·4 |
| 545 | 4·25 | 18·4 | 18·4 |
| 548 | 4·7 | 20·4 | 20·5 |
| 549 | 4·7 | | |
| 550 | 4·75 | | |
| 553 | 4·75 | | |
| 560 | 4·4 | | |

### (3) Temperature of Reduction 229° C.    (Curve IV, fig. 1.)

| Temperature. | Volume of hydrogen in 30 seconds. | Gramme-molecules of alcohol decomposed per second per gramme-atom of copper × 10³. | |
|---|---|---|---|
| ° abs. | c.c. | Observed. | Calculated. |
| 514 | 2·1 | 9·10 | 9·0 |
| 518 | 2·9 | 12·6 | 12·6 |
| 520 | 3·4 | 14·7 | 14·8 |
| 523 | 4·2 | 18·2 | 18·1 |
| 528 | 5·7 | 24·7 | 24·7 |
| 530 | 6·3 | 27·3 | 29·5 |
| 534 | 7·2 | 31·2 | |
| 537 | 9·2 | 39·9 | |
| 539 | 10·4 | 45·1 | 52·6 |
| 545 | 12·3 | | |
| 549 | 13·8 | | |
| 554 | 13·8 | | |

### (4) Temperature of Reduction 194° C.    (Curve II, fig. 1.)

| Temperature. | Volume of hydrogen in 30 seconds. | Gramme-molecules of alcohol decomposed per second per gramme-atom of copper × 10³. | |
|---|---|---|---|
| ° abs. | c.c. | Observed. | Calculated. |
| 498 | 0·5 | 2·16 | 2·16 |
| 500 | 0·6 | 2·60 | 2·57 |
| 507 | 0·9 | 3·90 | 4·31 |
| 512 | 1·4 | 6·07 | 6·07 |
| 517 | 2·1 | 9·10 | 9·00 |
| 522 | 2·9 | 12·6 | 12·6 |
| 525 | 4·0 | 17·3 | 16·1 |
| 530 | 5·2 | 22·5 | 22·4 |
| 533 | 6·4 | 27·7 | 27·7 |
| 536 | 7·7 | 33·4 | 33·9 |
| 539 | 9·2 | 39·9 | 41·0 |
| 542 | 10·3 | 44·6 | |
| 545 | 9·8 | | |
| 548 | 9·5 | | |
| 550 | 9·2 | | |
| 554 | 9·1 | | |

### (5) Temperature of Reduction 156° C.    (Not shown in figure.)

| Temperature. | Volume of hydrogen in 30 seconds. | Temperature. | Volume of hydrogen in 30 seconds. |
|---|---|---|---|
| ° abs. | c.c. | ° abs. | c.c. |
| 502 | 1·0 | 532 | 7·5 |
| 509 | 1·1 | 534 | 8·2 |
| 515 | 1·5 | 542 | 9·4 |
| 520 | 2·8 | 545 | 9·0 |
| 525 | 4·3 | 550 | 9·3 |
| 529 | 5·9 | 561 | 10·0 |

B. *Reduction of the Copper Oxide with Methyl Alcohol Vapour.*

A small distilling flask was sealed on to the top of the reaction tube in the position of the delivery tube for carbon monoxide or hydrogen. Pure anhydrous methyl alcohol was drawn into the flask when the reduction temperature in the reaction tube was reached. A slow current of nitrogen was passed through the flask and the methyl alcohol gently boiled by an external heating coil. On opening the lowermost tap of the apparatus the stream of vapour was carried through the reaction tube over the oxide. The minimum temperature of reduction for methyl alcohol vapour was found to be 205° C.

The catalytic effects of the catalyst prepared in this way are summarised in Table II :—

Table II.—Catalyst prepared by Reduction with Methyl Alcohol Vapour :
Anhydrous Ethyl Alcohol as reacting substance.

(1) Temperature of Reduction 217° C. (Curve X, fig. 2.)

| Temperature. | Volume of hydrogen in 30 seconds. | Temperature. | Volume of hydrogen in 30 seconds. |
|---|---|---|---|
| ° abs. | c.c. | ° abs. | c.c. |
| 501 | 0·9 | 527 | 6·8 |
| 504·5 | 1·2 | 532 | 7·2 |
| 511 | 2·35 | 534 | 7·4 |
| 518 | 4·1 | 539 | 7·9 |
| 522 | 5·8 | 542 | 8·9 |

(2) Temperature of Reduction 220° C. (Curve IX, fig. 2.)

| Temperature. | Volume of hydrogen in 30 seconds. | Temperature. | Volume of hydrogen in 30 seconds. |
|---|---|---|---|
| ° abs. | c.c. | ° abs. | c.c. |
| 522 | 3·0 | 540 | 7·0 |
| 524 | 3·6 | 544 | 8·2 |
| 527 | 3·8 | 546 | 8·5 |
| 534 | 5·6 | 549 | 8·6 |
| 537 | 6·4 | | |

(3) Temperature of Reduction 240° C.   (Curve VIII, fig. 2.)

| Temperature. | Volume of hydrogen in 30 seconds. | Temperature. | Volume of hydrogen in 30 seconds. |
|---|---|---|---|
| ° abs. | c.c. | ° abs. | c.c. |
| 518 | 0 ·70 | 540 | 6 ·70 |
| 522 | 1 ·50 | 544 | 7 ·6 |
| 527 | 2 ·50 | 547 | 7 ·9 |
| 530 | 3 ·65 | 549 | 7 ·9 |
| 534 | 4 ·75 | 552 | 7 ·9 |
| 537 | 5 ·75 | | |
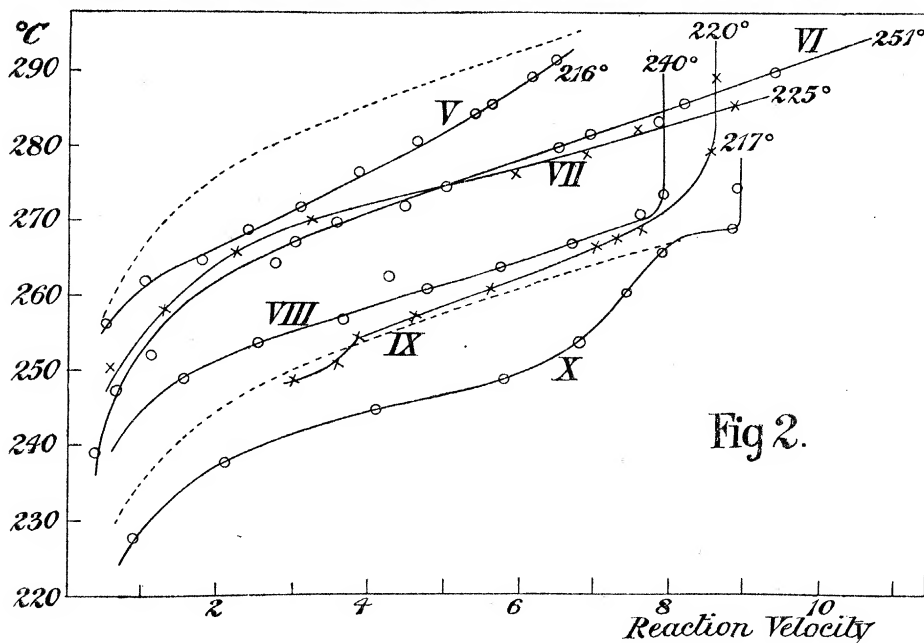


Fig 2.

*C. Experiments with Isopropyl Alcohol as the Reacting Substance.*

The alcohol used was a mixture of an old stock made from acetone by Sabatier's method with a new sample made by reducing acetone with sodium; this sample was supplied to me by the kindness of Mr. H. A. Scarborough.

The mixed samples were fractionated to within 0·1° C. by using a Dufton column.   The constants of the alcohol then showed very satisfactory agreement with the established values for the constant-boiling mixture of *iso*propyl alcohol and water.   Owing to the well-known difficulty of removing the last traces of water from this alcohol, its dehydration was not attempted.   It was considered more satisfactory to ensure that all the vapour passing through the reaction tube should be of constant composition than to use a partially dehydrated alcohol, giving a vapour of variable composition.

Owing to lack of time, the hydrogenation of this alcohol was studied only with the catalyst prepared with methyl alcohol vapour. The results show a general agreement with those for ethyl alcohol when the catalyst had been prepared with methyl alcohol or carbon monoxide.

Table III.—Catalyst prepared by reduction with Methyl Alcohol Vapour: Isopropyl Alcohol with 12 per cent. of Water as Reacting Substance.

(1) Temperature of Reduction 225° C. (Curve VII, fig. 2.)

| Temperature. | Volume of hydrogen per 30 seconds. | Gramme-molecules of alcohol decomposed per second per gramme-atom of copper × $10^3$. | |
| --- | --- | --- | --- |
| | | Observed. | Calculated. |
| ° abs. | c.c. | | |
| 513 | 0·5 | 2·17 | 2·0 |
| 520·5 | 0·65 | 2·82 | 3·1 |
| 525 | 1·1 | 4·77 | 4·6 |
| 531·5 | 1·35 | 5·85 | 6·0 |
| 537·5 | 2·75 | 11·9 | 11·1 |
| 540 | 3·2 | 13·9 | 13·5 |
| 543 | 3·55 | 15·4 | 15·4 |
| 545 | 4·45 | 19·3 | 19·0 |
| 553 | 6·5 | 28·2 | 27·6 |
| 557·5 | 6·9 | 29·9 | 30·0 |

(2) Temperature of Reduction 216° C. (Curve V, fig. 2.)

| Temperature. | Volume of hydrogen per 30 seconds. | Temperature. | Volume of hydrogen per 30 seconds. |
| --- | --- | --- | --- |
| ° abs. | c.c. | ° abs. | c.c. |
| 529·5 | 0·5 | 554·5 | 4·60 |
| 538 | 1·75 | 558 | 5·35 |
| 541 | 2·35 | 561 | 5·90 |
| 545 | 3·05 | 563 | 6·10 |
| 550 | 3·80 | 566 | 6·60 |

(3) Temperature of Reduction 251° C. (Curve VI, fig. 2.)

| Temperature. | Volume of hydrogen in 30 seconds. | Temperature. | Volume of hydrogen in 30 seconds. |
| --- | --- | --- | --- |
| ° abs. | c.c. | ° abs. | c.c. |
| 522 | 0·90 | 551 | 5·0 |
| 526 | 1·10 | 556 | 6·4 |
| 531·7 | 2·00 | 559 | 7·0 |
| 538 | 2·8 | 563·5 | 7·9 |
| 542·2 | 3·8 | 566 | 8·4 |
| 547 | 4·3 | 573 | 9·6 |

These results are shown graphically in figs. 1 and 2.

*Discussion of the Results.*

1. It will be seen that the activity of the catalyst does not necessarily increase continuously as the temperature of preparation from the oxide is lowered.

The order of activity is as follows :—

Temperature of reduction ° C.

(Carbon monoxide)
fig. 1.

215

229        Ethyl alcohol as reacting substance.

194

243        (The curve for preparation at 156° will be discussed later.)

(Methyl alcohol
vapour) fig. 2.

251

225        (Anomalous above 270°.)

217        Isopropyl alcohol as reacting substance.

This result conflicts with the view that the real catalytic agent is an oxide of copper dissolved in reduced (metallic) copper, but it could be readily reconciled with the theory put forward in the previous paper; namely, that metallic copper produced by reduction of cuprous oxide is the active agent. The proportion of active material formed by reduction would depend on the mutual relation of the velocity curves for the two reactions

$$CuO + H_2 = Cu + H_2O ; \qquad 2CuO + H_2 = Cu_2O + H_2O.$$
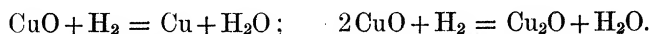
In support of this hypothesis, it may be mentioned that copper reduced from cuprous oxide is more readily attacked by ordinary reagents than metal produced from cupric oxide.[*]

It will appear from the later discussion that the inactivity of " cupric " copper is to be attributed to its lack of adsorbing power for alcohol, and not to any other cause.

2. The curves numbered in the figures 1 and 2, I, II, III, IV, VI, VIII, VII (below 270°), strictly conform to the relation $v = Ae^{-K/T}$ up to the point where the sudden change of direction occurs. Values of $v$ calculated from this law are shown in the last column of the above Tables.

$Log_e v$ was plotted against $1/T$, and from the resulting straight lines the following values were obtained :—

_____

[*] Private communication from Mr. E. K. Rideal.

Table IV.

Reducing agent, carbon monoxide : ethyl alcohol as reacting substance.

| Reduction temperature. | K. | $\log_e A.$ | Activity coefficients. | $v\,260°\,C. \div v\,250°\,C.$ (from $\log_e v$ values). |
|---|---|---|---|---|
| ° C. | | | | |
| 215 | 19,380 | 46·90 | $2\cdot4 \times 10^{-3}$ | 2·00 |
| 229 | 19,360 | 46·76 | $2\cdot1 \times 10^{-3}$ | 2·00 |
| 194 | 19,390 | 46·5 | $1\cdot6 \times 10^{-3}$ | 2·00 |
| 243 | 14,230 | 35·9 | $4\cdot0 \times 10^{-8}$ | 1·67 |

Reducing agent, methyl alcohol vapour : isopropyl alcohol as reacting substance.

| 251 | 19,490 | | $4\cdot8 \times 10^{-4}$ | 2·01 |
|---|---|---|---|---|

The simplest way of interpreting this temperature-velocity law would consist in imagining the catalytic process to resemble the thermionic emission of electrons from hot metals.

The active surface of the catalyst is to be regarded as covered with a layer of alcohol several molecules deep. Decomposition of alcohol, however, only occurs (to any measurable extent) in the layer in immediate contact with the catalyst. "Activation," that is, the absorption of energy necessary before reaction occurs, is brought about by absorption of radiation from the atoms of the catalyst. It is assumed that only in the layer of alcohol molecules next to the catalyst is the intensity of this radiation sufficient to bring about activation. This view receives support from the effect of adsorbed hydrogen on the catalyst to be discussed at a later point. Also, it appears to harmonise the hitherto opposed views of catalysis—the "physical" adsorption theory which made no allowance for the specific action of catalysts, and the "chemical compound" theory against which much has been urged. On the theory advanced above the specific action of the catalyst lies not only in selective adsorption but in providing radiation of the proper quality. Langmuir* has indicated that collision between gaseous molecules and a solid differs from ordinary kinetic collision in a homogeneous gas phase in being comparatively inelastic. The colliding gas molecule therefore sojourns on the surface of the catalyst for a period long compared with that occupied in ordinary "gaseous" collision and increased opportunity is given for activation. Herein lies the essential difference between catalysed and uncatalysed reactions.

* 'Phys. Rev.,' vol. 8, p. 149 (1916).

On the basis of these views a very simple explanation can be given of the sudden change in direction of the curves at temperatures approximately between 265° and 275° C.

While the alcohol film remains several molecules deep, catalytic action is independent of the rate of effective condensation on the catalyst, since the ranks of molecules always remain closed. As the temperature is increased the thickness of the adsorbed layer diminishes owing to the increased rate of evaporation, and at about 270° C. the film is only about two molecular diameters or less in thickness.

The rate of decomposition will now become dependent on an additional factor—the time-difference between condensation and evaporation of an alcohol molecule. Practically nothing is known concerning this time-difference or "life" of a molecule on a solid surface, but the effect on the catalytic activity of its variation with temperature might be indicated in a hypothetical extreme case by supposing the "life" of a molecule to be given by

$$\pi = Be^{aT},$$

where B and $a$ are constants.

Then the catalytic activity is given by

$$v = ABe^{-K/T} \cdot e^{aT} = ABe^{-aK},$$

that is, the catalytic activity is independent of the temperature. The curves indicate a very great decrease of the temperature coefficient and in some cases (as in curves I, II, XI, XII, figs. 1 and 3) even a decrease of the actual catalytic activity, due to the introduction of a new factor as indicated.

In column 4 of Table IV are shown a series of numbers called activity coefficients, calculated in the following way. The maximum number of alcohol molecules that could be condensed in a layer one molecule deep on one gramme-atom of copper would be the Avogadro number $N = 6 \cdot 06 \times 10^{23}$, assuming all the copper atoms could each adsorb one molecule of alcohol. A measure of the maximum number of alcohol molecules activated by the catalyst is given by the value of A in the equation

$$v = Ae^{-K/T}.$$

The activity coefficients show the value of the ratio $A/N$, which measures the combined effect of number of "active" copper atoms and the number of effective condensations.

The curves for *iso*propyl alcohol show no sudden change in direction up to 300° C.; presumably, the layer of this alcohol remains more than two molecular diameters thick above this temperature.

3. If the quantum theory of radiation is adopted, we may write

$$\frac{Nh\nu}{R} = K,$$

where the symbols have their usual significance, and K is given by

$$v = Ae^{-K/T}.$$

For the curves II, III, IV, VI (figs. 1 and 2)

$$\nu = 4\cdot04 \times 10^{14}, \qquad \lambda = 0\cdot742\,\mu.$$

For curve I (fig. 1)
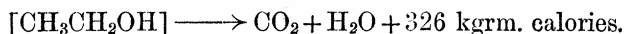
$$\nu = 3\cdot00 \times 10^{14}, \qquad \lambda = 1\cdot0\,\mu.$$
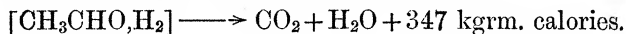
The heat of activation of alcohol in calories is given by

$$RK = 1\cdot98 \times 19,380 = 38,740 \text{ calories per gramme molecule.}$$

This value may be used to calculate the heat of activation of the reversed reaction, aldehyde + hydrogen → alcohol, by using Haber's relation

$$\Sigma Nh\nu \text{ (reactants)} - \Sigma Nh\nu \text{ (resultants)} = \text{heat of reaction.}$$

The heat of reaction may be found in the usual way :—

$$[CH_3CHO, H_2] \longrightarrow CO_2 + H_2O + 347 \text{ kgrm. calories.}$$

$$[CH_3CH_2OH] \longrightarrow CO_2 + H_2O + 326 \text{ kgrm. calories.}$$

giving

$$CH_3CHO + H_2 = CH_3CH_2OH + 21 \text{ kgrm. calories,}$$

whence the total heat of activation of the system [aldehyde + hydrogen] is 17 kgrm. calories, or approximately half the value for alcohol. Hence the hydrogenation of aldehyde requires $\lambda$ = approximately $1\cdot6\,\mu$.

The infra-red spectrum of copper shows absorption bands at $\lambda = 0\cdot8\,\mu$ and at $\lambda = 1\cdot6\,\mu$, so that the catalyst could provide the proper frequencies for both reactions, the lower frequency being more strongly developed at lower temperatures.

These considerations suggest an explanation of the commonly observed fact that metallic catalysts can operate in either direction of a reversible reaction according to the temperature.

### *The Effect of " Foreign " Substances Adsorbed on the Catalyst.*

The curves numbered V, X in fig. 2 depart markedly, and VII and IX slightly, from the simple logarithmic form, in the direction of increased activity between certain temperatures.

This abnormality is most marked with catalyst material prepared by a reducing agent that gives water as a product of reduction, namely, hydrogen and methyl alcohol, and increase in the effect is also shown by reduction at comparatively low temperatures.

It was thought that water might be retained by the catalyst in these cases and exert a strong specific catalytic action. To test this supposition, a number of curves were obtained for constant-boiling mixtures of various alcohols with water. These are shown chiefly in fig. 3. The broken line
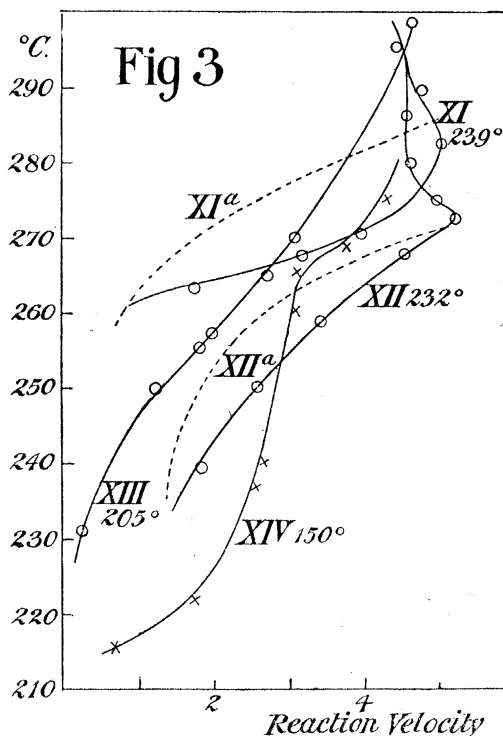


curves indicate the course of the simple logarithmic law. It will be noticed (in fig. 2) that, when *anhydrous* ethyl alcohol is used, a catalyst prepared with methyl alcohol at a temperature above 220° does not retain water, but, in spite of this, curves XI and XII show that water can be adsorbed on the catalyst from the reaction mixture (roughly in proportion to the amount present) even when the catalyst has been prepared at temperatures of 232° C. and 239° C. When isopropyl alcohol with 12 per cent. of water is used as reacting substance, water is apparently not retained on the catalyst if this is prepared above a temperature of about 216° (curve V), although curve VII shows a very slight deviation from the law, which is strictly obeyed by curve VI. The following is a list of the aqueous reagents, with the appropriate curves:—

Ethyl alcohol + 4·5 per cent. water (curve XII, fig. 3).

Normal propyl alcohol + 28 per cent. water (curve XI, fig. 3).

Isopropyl alcohol + 12 per cent. water (curves V, VI, VII, fig. 2).

This "promoter" effect of water could be predicted on the radiation theory, since the chemical similarity of water and the aliphatic alcohols would lead to similar spectra in the infra-red region.

The curve for reduction by carbon monoxide at a temperature of 156° (not given in figure) shows a slight departure from the logarithmic law, presumably due to traces of water in the ethyl alcohol.

The two curves for hydrogen reductions (*loc. cit.*) are included in order to discuss them in the present connection (curves XIII, XIV, fig. 3).

The low activity of the catalyst prepared by hydrogen must be attributed to the well-known retention of hydrogen by the reduced copper, which is consequently "poisoned." The catalyst is not completely covered with hydrogen, as the "water-effect" is very marked on both curves. Hydrogen has absorption bands in the infra-red at $0.6\,\mu$ and at $1.2\,\mu$, so that it would not be expected to act as a catalytic agent in the dehydrogenation, nor apparently is the radiation from the underlying copper able to act to any considerable extent on alcohol molecules across the hydrogen layer.

The work is being continued, with a view to finding the effect of admixed metals and oxides on the catalyst.

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# A Reciprocating Expansion Apparatus for Detecting Ionising Rays.

By TAKEO SHIMIZU.

(Communicated by C. T. R. Wilson, F.R.S. Received June 4, 1921.)

The present investigation was undertaken for the purpose of obtaining a very sensitive method of detecting ionising rays, such as X-rays and rays from radio-active substances. An electroscope or electrometer, in combination with an ionisation chamber, even if the required sensitiveness were obtained, would not distinguish between the effects of a single ray and of two or more which entered the chamber simultaneously. In order to attack certain problems relating to the structure of ethereal waves and other delicate questions, it is necessary to have some means of detecting and discriminating individual rays. Mr. C. T. R. Wilson's beautiful method of making visible the tracks of ionising rays in gases* affords us the most powerful means for that purpose, and the writer accordingly tried to obtain a modified form of the original apparatus, such as could be readily used for various experiments.

* 'Roy. Soc. Proc.,' A, vol. 87, pp. 277–292 (1912).